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From Box 8-3-35

MATERIAL BALANCE

ORGDP



## Purpose

The purpose of this material balance is to determine how much technetium has entered the plant, how much has left the plant, and how much has accumulated at the plant from 1953 through 1977. During recent years, all incoming and outgoing streams have been monitored. However, in the early years, very little data exists. This means that in order to obtain a material balance, certain assumptions will have to be made when analyzing the data. ~~The data~~ ~~used~~ ~~in~~ ~~current~~ ~~through~~ ~~December 31, 1977.~~

## Introduction

Technetium-99 is a fission product which has been fed to the diffusion plants primarily from government reactor return material. During the manufacture of uranium hexafluoride ($UF_6$), the chemistry of the process is such that the traces of technetium present in the starting material will probably be largely found as $TcF_6$ and $TcO_3F$ in the $UF_6$ feed. Being a light element compared to uranium, it tends to concentrate in the top of the cascade. Laboratory studies have shown that both $TcF_6$ and $TcO_3F$ will sorb on equipment surfaces with $TcO_3F$ being more strongly sorbed than $TcF_6$.[1,2] Since $TcF_6$ is more unstable than $TcO_3F$, it will react with $UO_2F_2$ (the product of hydrolysis of $UF_6$) to form $TcO_3F$ and a non-volatile technetium fluoride compound. On the other hand, $TcO_3F$ is realitvely stable toward $UO_2F_2$. The chemical behavior of $TcF_6$ and $TcO_3F$ indicates that there will be a difference in the disposition of these compounds in a diffusion cascade. $TcO_3F$ will probably be sorbed on equipment surfaces and the $TcF_6$ will move more rapidly through the cascade with some conversion to $TcO_3F$ when it contacts $UO_2F_2$.



Also Power

of Tc largely sorbed on casc equip- (Sect VIII) then how much equip removed in old C/P - thus how much Tc lost at that time? Sect VII makes pt of removing Tc with equip then in decont - if 50% left on barrier (which I doubt) then residues from old C/P after barrier converted to Ni powd must have lots of Tc.

Input

Technetium has entered the plant from three sources: government reactors, Paducah product, and commercial reactors. The main source of technetium has been government reactors, since the technetium in Paducah product originates from government reactors and the commercial reactor material amounts to less than 0.02% of the total received at ORGDP. As can be seen from Table 1, the government reactor material has come from two sources: Hanford and Savannah River.

Table 1

TECHNETIUM RECEIVED

| Source of Technetium | Amount Received in kg |
|---|---|
| Paducah Product | 117 |
| Savannah River | 56 |
| Hanford | 30 |
| Commercial Reactors | < .04 |
| TOTAL | 203 |

Paducah product has been fed to the plant over the past 25 y. Analysis of this product has ranged ~~a high of~~ from 20 ppm to ~~a low of~~ less than 0.1 ppm. Data on the analysis of the Paducah product is available from 1960 ~~forward~~ to the present. Very little data is available previous to 1960. A summary has been prepared by PGDP which lists the quantities of technetium shipped to ORGDP[3]. It is estimated that 117 kg of technetium ~~has~~ have been received from PGDP. This number was obtained by ~~weighing~~ weighting the quantity of $UF_6$ shipped to ORGDP from PGDP according to the average technetium concentration for that time span. Since these average values are based on limited data, the quantity projected ~~is~~ maybe subject to ~~considerable~~ error. ~~The following tables~~, provided by S. F. Seltzer, outline the amount of PGDP product shipped to ORGDP, the average amount of technetium in that product, and the amounts of technetium received from PGDP.

Tables 2, 3, and 4

Table 2

DISTRIBUTION OF PGDP PRODUCT $UF_6$

| Period | PGDP Product U Shipped to ORGDP (kg x $10^6$) |
|---|---|
| 1953-1962 | 33.05 |
| 1963-1965 | 7.24 |
| 1966-1971 | 14.48 |
| 1972 | 3.45 |
| 1973 | 1.96 |
| 1974 | 2.23 |
| 1975 | 0.18 |
| 1976-1977 | 4.73 |
| | 67.32 |

Table 3

AVERAGE Tc CONCENTRATIONS IN PGDP PRODUCT $UF_6$

| Period | Avg. Tc Concentration, ppm U Basis |
|---|---|
| 1953-1962 | 2.28 |
| 1963-1965 | 0.66 |
| 1966-1971 | 0.66 |
| 1972 | 0.67 |
| 1973 | 4.10 |
| 1974 | 6.10 |
| 1975 | 1.00 |
| 1976-1977 | 0.66 |

Table 4

DISTRIBUTION OF Tc IN PGDP PRODUCT $UF_6$

| Period | Kilograms Tc Shipped to ORGDP |
|---|---|
| 1953-1962 | 75.35 |
| 1963-1965 | 4.78 |
| 1966-1971 | 9.56 |
| 1972 | 2.31 |
| 1973 | 8.04 |
| 1974 | 13.60 |
| 1975 | 0.18 |
| 1976-1977 | 3.12 |
| | 116.94 |

Technetium received from government reactors has been estimated at 86 kg. This figure was determined by estimating 5 g per ton (∿7ppm on U basis) of $UO_3$ received. This estimate was obtained from R. F. Smith[4] (PGDP) and is in agreement with the available data at ORGDP. Fifty six kilograms have been received from Savannah River and 30 kg from ~~the~~ Hanford. ~~Reactor~~. The ~~only other~~ third source of technetium at ORGDP is commercial reactor returns. According to a recent survey, 465 MTUA (metric tons Uranium) of commercial reactor material[5] ~~has~~ have been received at ORGDP. Laboratory analyses have shown this material to contain an average of 0.08 ppm which would mean that a total of less than 0.04 kg ~~has~~ have been received. This ~~amounts to~~ is less than 0.02% of the total received and ~~has~~, therefore, has been treated as a negligible quantity. Since this quantity is based on analyses for 1 y (1977) and assumed to be the same over a 7-y period, ~~considerable~~ some error in calculating the total quantity may have been introduced. However, if the concentration of technetium were

considered at the maximum allowable value (4 ppm), it would still amount to less than 1% of the total already computed and would still be negligible from a material balance viewpoint.

If the amount of technetium received is viewed on a year-by-year basis, the difficulties in doing a material balance quickly become obvious. According to Table 4, 75.35 kg of the technetium from PGDP were received by 1962. All of the government reactor UO3 had been received at ORGDP by this time. This means that nearly 80% of the technetium received at ORGDP was received prior to 1962. During this period of time very little data was collected, so the uncertainty in the quantities stated could be significant.

Output

Data on the exit streams from ORGDP is very limited. Only in the past four years have routine analysis of the exit streams been conducted for technetium. It is difficult to reconstruct operating conditions throughout the cascade in past years. Therefore, to determine a material balance, present operating conditions have to be assumed to reflect those of the past. Quantities presented in this section based on the given assumptions are subject to a rather large error.

During past years technetium could have been released to the atmosphere through two outlets: purge cascade vent and the K-1131 stack. Routine analysis on the first exit, the purge cascade vent, are available for a 4-y period, 1974-1977. During 1977 a KOH scrubber was installed on the purge cascade vent. This scrubber has effectively removed the technetium from the exit stream. Since this scrubbing system will remain in operation, data collected on future years should closely correspond to 1977. The amount of technetium released during 1977 was 1 x $10^{-6}$ ci. The data

collected for 1976 was rather high. This reflects the adjustments to and experimentation on the purge cascade vent. Hoever, this data was averaged with the available data from 1974 and 1975 to obtain a value of 2.54 ci per y. Over a ~~25~~ 26-y period this would amount to approximately 4 kg released to the atmosphere. This is a ~~most~~ difficult estimate to make because the quantity released would be assumed to peak in the late 1950's or early 1960's, since the majority of the technetium received at ORGDP had entered the plant by that time. Also the trapping system has varied somewhat during past years.

The second source of technetium released to the atmosphere was the K-1131 stack. This material originated from the conversion of $UO_3$ from government reactors to $UF_6$. This facility ~~is no longer in operation~~ was discontinued in the early sixties. PGDP has estimated that 5% of the technetium in the $UO_3$ is vented to the atmosphere during the fluorination of the $UO_3$. If it is assumed that the facility at ORGDP functioned in a manner similar to PGDP, then 4 kg of technetium ~~was~~ were vented to the atmosphere. There is no available data on this stack.

During the decontamination of equipment and the recovery of uranium, the majority of the technetium has been shown to follow the raffinate. Analyses of the recovered uranium during 1977 showed a total of 0.008 ci technetium. Assuming that this data is typical of past years, a total of 12 gm left the plant in recovered uranium. From a material balance viewpoint this amount is negligible.

The raffinate has been routinely analyzed during the past 4 y, 1974-1977. The majority of this material goes to the K-1407-B pond, although during 1977, a portion of this material was shipped to Y-12. The material shipped to Y-12 amounted to 8.85 ci of technetium. The available data is somewhat scattered with 2 y showing a value of ~20 ci and 2 y showing lower values (~4 ci). However, a scattering of data would be expected since the amount of technetium in the raffinate is dependent upon the amount of equipment changed out in a given year, which will have considerable variance from year to year. Therefore, it would be a fair assumption that the data collected over this 4-y period is typical throughout the history of ORGDP. This data was averaged to obtain a quantity representative of that released during any of the years in the past. An average

value of 11.63 ci per is used over a 25-y period to obtain a value of approximately 18 kg technetium leaving the cascade through this exit stream. It is felt that the value of 11.63 takes into consideration the fact that in early years it was much less and that during the changeout programs in the 1950's and 1960's it may have been much higher.

Another outlet of the technetium from the cascade is in the product. Like the other exit streams, data on the product is rather limited. Routine analyses are available ~~over~~ for the past 2 y (1976-1977) with scattered data available previous to this time ~~period~~. In reviewing the available data, it is apparent that there is a direct relationship between the technetium being fed to the cascade and the amount of technetium in the ORGDP product. During periods of time when very little technetium ~~is~~ being fed to the cascade, very little ~~is~~ seen in the product, and when larger quantities ~~have been~~ fed, larger quantities ~~are~~ seen in the product. During 1977 an approximate decontamination factor of 4 was observed across the cascade. In 1975 this value was shown to be 3.3 and in 1972 it was 4.0. ~~If it can be assumed~~ that the ORGDP cascade exhibits a decontamination factor of approximately 4, then, based upon the concentrations of technetium being fed and the amount of product withdrawn, a quantity of technetium leaving ORGDP in the product can be determined. PGDP product ~~has been shown to~~ average 1.7 ppm over the 25-y period it was fed. This ~~would suggest a possible~~ 0.45 ppm average for ORGDP product. However, this must be adjusted upward since government reactor material accounted for approximately 42% of the technetium fed. Taking this into consideration, an average value of 0.61 ppm was obtained. This would mean that approximately 13 kg of technetium went into ORGDP product.

Accumulation

The input less the output equals the accumulation of technetium on plant-site. The accumulation section includes the cascade equipment, the burial grounds, and the technetium containing materials stored at ORGDP. ~~Very~~ few analyses exist for these materials at ORGDP, making it nearly impossible to assign quantities to the various areas.

At the purge cascade, a series of traps ~~are~~ installed. These consist of the NaF traps, the $Al_2O_3$ traps and the KOH scrubber. The purpose of these traps is to prevent the escape of $UF_6$ to the atmosphere.

The NaF traps sorb technetium as well as $UF_6$. However, when the traps become loaded with $UF_6$, they are desorbed back into the cascade. This desorbtion is accomplished at 700°F using a small stream of fluorine. During this desorbtion process, the technetium present is also flashed back into the cascade. This creates a closed loop in which only trace quantities of Tc pass through the NaF traps.

The NaF traps can be used through many cycles of sorbtion and desorbtion and are not changed out unless ~~it~~ ceases to function. On occasion these traps will be overheated, which causes the NaF to fuse. At this point the trap ceases to function and must be changed out. This overheating tends to drive off the technetium. However, laboratory analyses have shown that trace amounts remain (0.1 to 0.3 wt %) ~~with the NaF.~~

During 1977 approximately 200 lb of NaF material ~~was~~ changed out. ~~If~~ 1977 ~~can be assumed~~ to be a typical year and 0.2% ~~can be assumed~~ to be a typical loading, ~~then~~ approximately 4 kg of technetium ~~has~~ left the cascade via this mechanism. Spent NaF was originally dissolved at K-1420, but has for the past few years been stored at ~~K-25~~.

The $Al_2O_3$ traps are used throughout the cascade as well as at the purge cascade vent. Since the majority of the technetium is trapped out by the NaF traps and flashed back into the cascade at the purge cascade vent, very little technetium reaches the $Al_2O_3$ at this point. The other $Al_2O_3$ traps are located in the lower cascade where ~~very~~ little technetium exists. Although some technetium is removed by this mechanism, not enough data exists to affix a quantity to it. Due to the locations of the traps, this quantity is assumed to be negligible ~~amount~~. When this trap

material is taken from service, it is sent to K-1420 and surveyed. $Al_2O_3$ material is decontaminated and sent to the contaminated burial grounds.

Another place where technetium has accumulated at ORGDP is stored barrier. During the decontamination of converters removed from the cascade, the barrier is removed, decontaminated, cut into pieces, and stored in cannisters in the vaults at K-25. The decontamination of barrier is such that a significant quantity of Tc remains with the barrier. Laboratory results, although inconclusive, have indicated that as much as 50% of the Tc on the barrier may remain after decontamination. Therefore, it can be concluded that a significant quantity of Tc has been stored along with the barrier. This assumption is made because the source of Tc that has been recorded at K-1420 originates from the decontamination of equipment, barrier, and trap material with the majority coming from barrier. However, no analysis exists to substantiate the quantity that might be present.

During the early 1960's, ORGDP ceased to enrich uranium to the higher assay levels. This resulted in the closing of the K-25 building. Since the majority of the Tc fed to ORGDP had been fed by this time and since the nature of Tc is to move up the cascade, it is felt that a large quantity of Tc still remains in the K-25 building. Samples have been pulled to get an indicated of the quantity, but the large quantities of uranium on the barrier have made analysis difficult and the data is inconclusive at this time.

With the installation of the new purge cascade at K-402-9 during 1976, the old purge cascade at K-311-1 was shut down. Since the nature of Tc is to move up the cascade, a large quantity of Tc remains in the old purge cascade. It is impossible to determine how much is present at K-311-1 without the actual removal of equipment which is not feasible at this time.

Summary

The following table summarizes the data presented in this report.

Set up table differently

TABLE 5

Receipts — XXX
~~Dispositions~~ — ~~xxx~~
Vent Heels
~~Cascade~~ — ← then show where for cascade

→

TECHNETIUM MATERIAL BALANCE AT ORGDP

| | Kg |
|---|---|
| Total Received | 203 |
| Charged to Cascade | 179 |
| ~~Removed from Cascade~~ | |
| K-1131 Vent | 4 |
| Cylinder Heels | 20 |
| K-1420 Raffinate | 18 |
| Product | 13 |
| K-311-1 Purge Vent | 4 |
| Sodium Fluoride Traps | 4 |
| ~~Residual Accumulation~~ (Stored Barrier, K-65 Building, Operating Cascade, K-311-1 Purge Cascade, Burial Ground, ~~K-65 Scrap~~ Total Yard | 140 |

what happened to this difference

Indent

UNCLASSIFIED

The last remaining source of Tc at ORGDP is the operating cascade. A few analyses have been run in an attempt to determine the quantity of Tc in the cascade.[6] However, these are ~~very~~ limited to the barrier in the K-33 building, which is in the lower cascade. In order to determine the quantity of Tc in the cascade, a systematic study would have to be undertaken examining each area of the cascade. This data is not available at this time. Therefore, no quantity has been affixed, although a large quantity is believed to be in ~~this area~~ the operating cascade.

Summary See enclosed sheet

The input of Tc to ORGDP has been 203 kg. Of this quantity, 179 kg was actually fed to the cascade. This leaves 24 kg with 4 kg being emitted to the atmosphere at the K-1131 stack and 20 kg remaining in cylinder heels which circulate between ORGDP plant and PGDP. Of the 179 introduced into the cascade, 4 kg have been released to the atmosphere at K-311-1 purge cascade vent, 18 kg have left in the raffinate from K-1420, 13 kg have left in the product, and 4 kg have been removed by the NaF traps. This leaves 140 kg which is assumed to still be at ORGDP. This material is contained in one of the following:

1. Stored barrier
2. K-25 building
3. Operating Cascade
4. K-311-1 Purge Cascade
5. Burial Grounds

Recommendations

It is recognized that the data are limited and that any number presented is subject to a rather large error. Therefore, it is felt that certain recommendations be made. Since it is impossible to go back into the past and produce data that does not exist, every effort to accumulate data now and in the future should be made. If we are to provide better data, the following should be done:

1. Analyze Paducah product for Tc
2. Analyze our product more frequently for Tc
3. Analyze all trap material
4. Conduct a profile on the Cascade.

What are we recommending that we do?

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